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Sulfur containing optical plastics and its ophthalmic lenses applications

G. S. Jha,[1] G. Seshadri,[1] A. Mohan,[2] R. K. Khandal[1]*

[1*] Shriram Institute for Industrial Research, 19, University Road, Delhi-110007, India; fax: 91-011-27667676; e-mail: gsjha2000@yahoo.com
[2] Basic School of Applied Science, Guru Gobind Singh Indraprastha University, Delhi 110006, India; e-mail: amohan62@gmail.com

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Abstract: Plastics produced from the sulfur-based monomer are excellent materials with many optical applications such as ophthalmic lenses, fiber optics and non- linear optics. High refractive index plastic materials are able to reduce the curvature, edge and center thickness of lenses. Sulfur containing plastics such as sulfide, polysulfide, and sulfur containing vinyl compound, thioacrylate, polythiol and isocyanate/isothiocyanate based monomers have demonstrated high refractive index, high Abbe number, good impact strength, excellent machinability, good tintability and good transmittance. In the present article, various sulfur containing plastics with different types of monomers for ophthalmic lens applications are reviewed.
Keywords: Sulfur containing plastics, Optical application, Ophthalmic lenses, Refractive Index, Abbe number.

Introduction

As our understanding in recent years of materials increased, replacement of glass by alternate materials, such as plastics and polymers took place. The use of plastics as optical device started in the 20th century with the discovery of polymethyl methacrylate and polycarbonate [1]. These plastics lead to, the invention of sophisticated optical devices such as spectacles, contact and intraocular lenses, prism, optical fibers, substrates for an information recording medium and light emitting diodes [2]. Optical plastics produced from sulfur based compounds/monomers are excellent materials with high refractive index and high Abbe number. Use of optical plastic materials with high refractive index has increased many folds in present times. These high refractive index optical materials can dramatically reduce optics profile and make lens lighter and thinner [3-4]. The higher index material refracts light more efficient as they are denser with reduced edge thickness, weight and curvature. High refractive Index optical plastics have become the most promising candidates in present time's scenario of high-speed telecommunication, optical signal processing, optical computing and networking. In the present article we have reviewed the use of sulfur containing plastics in ophthalmic lens applications.

Optical plastics for ophthalmic lens applications should meet a number of requirements [5-12] such as high transparency, possibility to regulate refractive index [13-15] and resistance to atmospheric conditions during usage. Optical plastics have many other important properties such as the reflection, scattering, absorption, clarity, haze, & birefringence. The improved processability and other characteristics such as tintability make polymeric materials especially attractive as a material for ophthalmic lens [16]. The optical properties of a polymer have to be considered in evaluating its potential usefulness in a wide variety of applications such as compact disk coatings and lenses used in eyeglasses materials. In order to reduce the weight and increase the safety, glass has been replaced by plastics. High refractive index materials are used to minimize the problems related to the weight of the lens since such materials (n = 1.60 and above) can be used to reduce the weight of the optical material & thickness of lenses [17]. Some of the polymers having refractive index greater than 1.6 are polyvinylidene chloride (refractive index = 1.60), poly(pentachlorophenyl methacrylate), (refractive index = 1.60), poly(dichlorostyrene), polystyrene sulfide (refractive index = 1.65), polythiourethane (refractive index = 1.67) and poly (pentabromophenyl) methacrylate (refractive index = 1.71). High molecular weight PMMA and CR-39 are isotropic and homogeneous and retain properties when machined to shape and polished but have low refractive index [6-7]. For optical resins the refractive index and Abbe number are the most important properties.

Considerable research has been directed towards the development of polymers with a combination of properties, which make them well suited for optical applications. Generally, high refractive index is of principal importance for an optical material since the use of a high refractive index material allows production of thinner lenses while designing lenses of the same power. Reduction of edge thickness of the lens offers practical advantages in terms of weight saving and also aesthetic reasons [3]. In Figure-1 and Figure-2 are shown the edge thickness and curvature of ophthalmic lenses from normal and high refractive index materials.

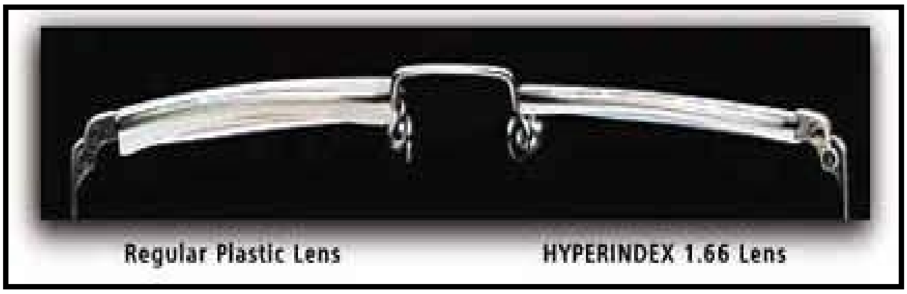


Fig. 1. Edge thickness of high refractive index low refractive index ophthalmic lens.

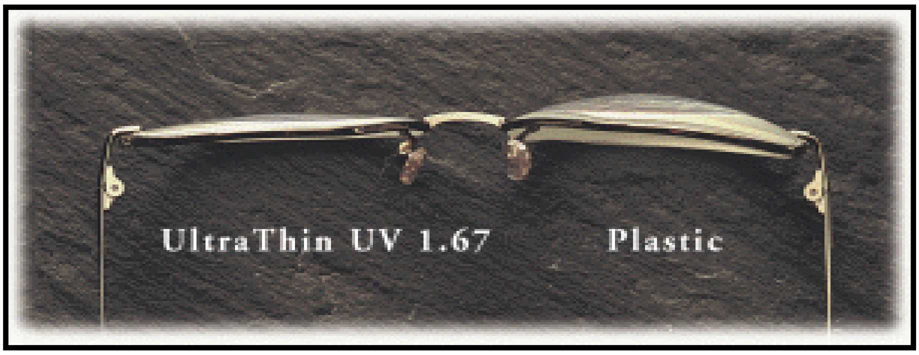


Fig. 2. Curvature of high refractive index low refractive index ophthalmic lens.

Another important consideration for optical materials is optical dispersiveness or Abbe number. The Abbe number typically characterizes the value of optical dispersiveness. Materials with high Abbe numbers show little less optical dispersive nature while materials with low Abbe numbers show high optical dispersive nature. A high Abbe number is desired for optical materials since this will lead to reduced chromatic aberration and better image clarity for a given lens design and thickness. Therefore, while using an optical material, it is very important to balance refractive index and Abbe number so that they both are suitable for the end product. Optimally, both refractive index and Abbe number should be high [20].

In order to obtain polymers with high refractive index and Abbe number, polymer were incorporated with certain characteristic structures [21-22] as an aromatic group [23-28], a halogenated aromatic group [29-35] and an alicyclic condensed ring [36], but refractive index and Abbe number were found to improve only moderately. Polyelectrolytes that are composed of specific organic polymer chains and inorganic moieties showed remarkably high refractive index and Abbe's values due to the latter compound [37]. By increasing the polarizability [38-42] of substitute groups, the refractive index of the resulting polymer can be increased. Therefore, by incorporating oxygen, sulfur or sulfoxide in the polymers high refractive index has been produced. Sulfur containing monomers are good candidates for producing high refractive index optical plastic materials, because the polarizability of the sulfur produces a strong interaction between materials and incident light resulting in high refractive index [43-45]. Based on molar refraction [46-53] and molar dispersion sulfur containing polymers should have higher refractive index and Abbe number values. For instance, polymer possessing, sulfide [54], S-alkyl ester [55] and S-alkyl carbamate [56-57] showed higher refractive index and Abbe values. It is well known that the latter polymers can an easily obtained by polyaddition of polythiol and polyisocyanate, which have high refractive index and Abbe numbers [56-58].

Thiol compound has high sulfur content, in which the atomic refraction is high and which therefore significantly affect the refractive index of the polymers. In general, the Abbe number of amorphous material decreases with the increase in the refractive index. One problem with polymers having high sulfur content is that the electron resonance of sulfur is remarkable, therefore, often significantly reducing the Abbe number [59-61]. Another cause of the increase in the refractive index is the decrease in the molar volume [55-57, 62]. This is often seen in polymers having a high cross linking density and a strong intramolecular force. The sulfur compound-containing polymer increases the refractive index due to decrease in the molar volume [63]. So sulfur containing plastic materials that can be used in the field of optics is increasing drawing attention of research in worldwide.

The advent of plastics lenses

During the early part of 20th century, major advances were associated with new kind of lens materials. With the expansion of organic and synthetic polymer chemistries, much of which was an outgrowth of material challenges overcome in World War II. It was soon discovered that optically clear materials could be made from polymers. Since that time, work has been done to develop a plastic lens material. Glass lenses, particularly those that correct vision problems were traditionally very heavy. The logic was that a plastic lens with optical properties similar to those of glass would be much lighter. Initial attempts to lower the weight of a given lens were in the late 1930s, using polymethyl methacrylate (PMMA). One major drawback of that material, however, was its inability to resist scratches. In fact, PMMA was so susceptible to scratches as plastic lens material that it turned into a commercial disaster. The first truly successful plastic lenses were introduced shortly after World War II. They were made from the thermosetting resin diallyl diglycol dicarbonate, commonly called ADC or CR-39. The inherent scratch resistance of this material, compared with other plastics at the time, as well as its impact resistance and low density, ensure its commercial success. Polycarbonate, a very tough thermoplastic, became widely available by the late 1980s. High refractive index resins derived from polythiourethane were later introduced to make lenses thinner and lighter [64-68].

Until 1992, the only high index materials available for ophthalmic use were dense barium flint, or extra dense flint glasses or titanium dioxide glasses with the refractive index in range 1.65 to 1.70. In 1992, Ashi Pentax introduced series of 1.66 index lenses made from the Matsui, MR-7 monomer. This was the first of series of high refractive index monomers, which were introduced by various major chemical companies in Japan. This culminated in the 1.71 monomer produced by Mitsubishi Gas Chemical Corporation and first marketed in 1997 by Hoya as its Teslalid material. The 1.71 index lens series in this material is now available from several other sources such as Essilor, Stylis, Eynoa, Kodak, Nikon, Rodenstock, Seiko, and Zeiss. Table-1 shows the history of development of optical plastics.

Tab. 1. History of development of optical plastics.

Years	Invention
1937	methyl methacrylate
~1942	diethylelene glycol bis (allyl carbonate) (CR-39)
1955	polycarbonate
1987	polythiourethane

Limitation of existing optical materials

Glass and plastics each has its own unique advantages. Generally, glass materials are harder and more durable than plastic. Glass is much heavier than plastic. The large selection of glass materials allows the designer to choose materials with desirable optical properties such as refractive index and dispersion to achieve better optical performance. This kind of freedom is limited with plastic materials. However, plastic optics offers other design freedoms that are not achievable or economical with glass optics. Glass lenses are made by grinding and polishing process where as precision plastic lens is made by injection molding and casting process. The difference in manufacturing process provides plastic optics some unique advantages such as high volume production capability and low manufacturing cost, design sophistication, unique design possibility and consistent quality. Plastic materials are more sensitive to environment changes such as temperature and humidity. In addition, the material flow pattern and shrinkage during molding also limit the surface accuracy that is achievable with plastic optics. The index distribution with in a mould component may be inhomogeneous and of varying polarization. The chemical properties of available high refractive index optical plastic materials also increase the performance by the optical coating that can be deposited on the plastic materials [69]. Some other advantages of optical plastics are as follows:

- Low density
- Low raw material cost
- Good impact resistance
- Excellent configuration flexibility
- High transmittance of incident light
- Safety involved in their use because when optical polymers break, the fragments tend to be large and obtuse and hence pose less danger
- Ease of application of surface coating (which is used to disperse light or create a contrasting appearance

A variety of polymeric materials including polycarbonates, polystyrenes, acrylic polymers, polythiourethane, and polysulfones have already been used for optical applications. Each of these materials offer a somewhat different combination of physical and optical properties, which lead to advantages and disadvantages for optical applications. For example, polycarbonate lenses typically show excellent impact resistance but are also characterized by poor scratch resistance and tintability and high chromatic aberration. CR-39 has low refractive index. Acrylic polymers have excellent optical clarity, but poor impact resistance and a relatively low refractive index. Polystyrenes are typically characterized by a relatively high refractive index, but also show a great deal of optical dispersion combined with poor impact resistance. Polysulfones have a high refractive index, but are typically colored. Polythiourethane have high refractive index, good impact resistantace and high Abbe number. Sulfur containing plastics are most popular materials for optical applications because of its better optical properties such as high refractive index and high Abbe number [70].

Optical properties

There are many optical characteristics such as refractive index, Abbe number, light transmission, light reflectance, specific gravity, impact strength etc. But refractive index and Abbe number are most essential properties for the material to be used for optical applications.

Refractive index

The most important property of optical material is the refractive index and its dispersion behavior. If light enters a non-absorbing homogeneous material reflection and refraction occurs at the boundary surface. Practically speaking the refractive index is a measure of Strength of deflection occurring at the boundary surface due to the refraction of light beam. Refraction and diffraction phenomenon of light is shown in Figure-3.

The refractive index is a measure of how much light is bent or refracted as it passes through a substance. It is defined by:

$$n = \frac{\sin i}{\sin r}$$

Where n is the refractive index; 'i' and 'r' are the angles of incidence and refraction respectively.

The refractive index is also the ratio of the velocity of light in vacuum to the velocity of light in any medium.

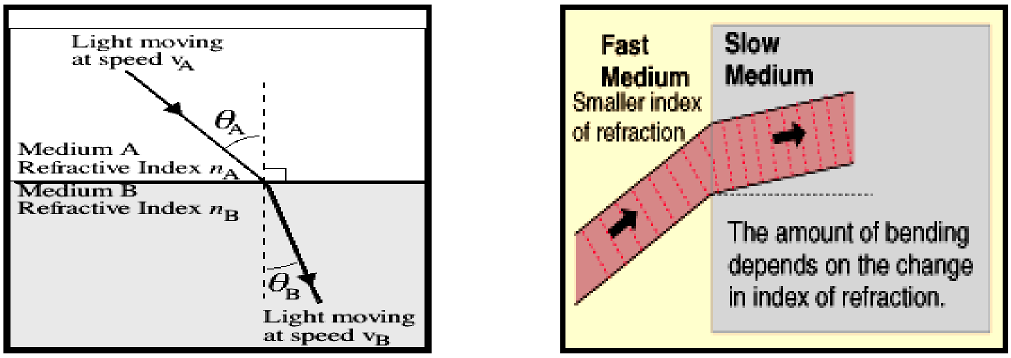


Fig. 3. Refraction and diffraction of light

Abbe Number

The variation of refractive index with the wavelength of light causes the phenomenon of chromatic dispersion of white light upon refraction. Since the refractive index is higher for short wavelengths, refraction of visible light spreads from the red zone towards the blue zone of the spectrum (Figure-4).

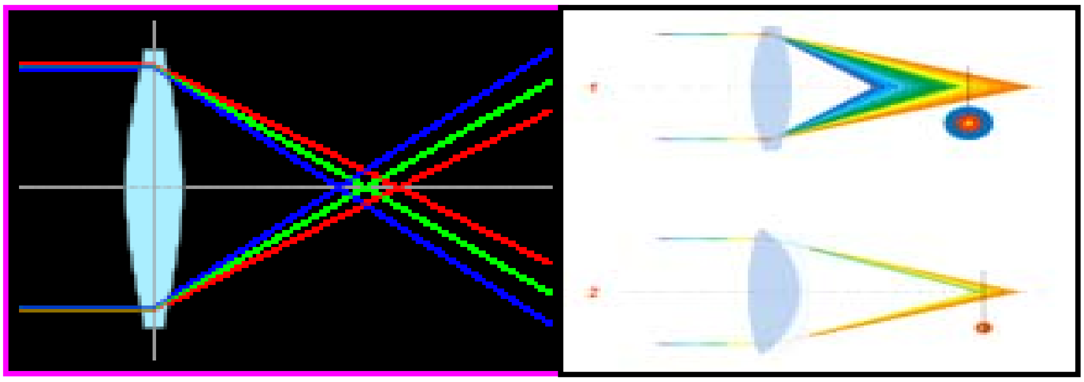


Fig. 4. Chromatic dispersion of light.

To characterize the dispersive power of the material, a quantity Abbe number is used with the following respective formulae

$$v_d = \frac{n_d - 1}{n_f - n_c}$$

Where n_d is the Refractive index for λ_d = 587.56 nm, d= 587.56 nm; n_f is the Refractive index for λ_f = 486.13 nm, f= 486.13 nm; n_c is the Refractive index for λ_c

= 656.27 nm, c= 656.27 nm; n_d, n_f and n_c are the refractive indices of the material at the wavelengths of Fraunhofer d-, f-, c- spectral lines.

The Abbe number is inversely proportional to chromatic dispersion of the material. The Abbe number varies between 60 for the least chromatic and 30 for the most chromatic materials.

Classification of sulfur containing optical plastics

In the last decade of the twentieth century, sulfur-containing polymers have increasingly come into attention because of their interesting properties that make them useful in a wide range of applications. They can be used as high performance engineering plastics, chemically stable ion-exchange membrane in electromembrane process, proton conducting electrolytes and optical, optoelectronics and photochemical materials. Sulfur polymers are used as bio-membranes and blood compatible materials. Polysulfates and polysulfonates are used as antiviral agents [71-74].

Developments of sulfur containing plastics are being explored for their commercial exploitation because of their certain unique characteristics like high refractive index, stiffness and stability towards oxidation. Sulfur containing polymers must include polymers with very different repeating units. In some cases it may be possible to state that the –s- bridges introduce a certain flexibility, where as in others –s- units introduce stiffness and hence enhance stability toward oxidation. Thus, sulfur atoms are present in various valance states and contribute in different ways to the inherent polymer properties. Consequently sulfur-containing polymers vary from highly reactive to chemically inert substance, can have high softening points or can be viscous oils. Some of these polymers have found commercial application, where as others are of academic interest.

This review gives an insight into sulfur containing optical plastics classified on the basis of functional groups attached in polymer chain. Some of these classes, such as polysulfones, polysulfides and isothiocyanate have been reviewed [72]; however their optical applications have not been discussed. Indeed, a comprehensive review on sulfur containing optical plastics includes polymers with very different type of sulfur repeating groups.

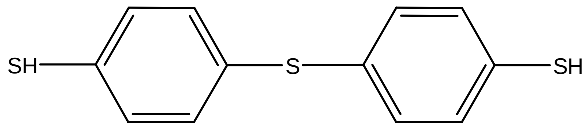
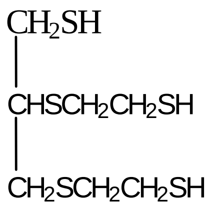
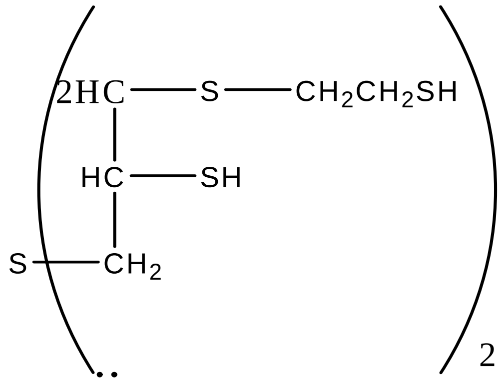
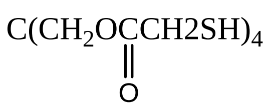
The classifications of optical plastics in this article include sulfur atom joined to the monomer and useful for optical applications. It is possible to state that – S – bridges introduced a certain flexibility, increase the refractive index due to higher molar refraction of C – S, S – H and S – O bond, whereas – S – units introduce stiffness and enhanced stability towards oxidation, although this is by means applicable to all the polymers involved. The classification based on sulfur compound/monomers attached or incorporated to polymer resins are as follows:

Metal sulfides

Polymers that contain inorganic particles such as metal sulfide are widely used in technology. In most cases the inorganic articles either enhance the mechanical properties of polymer or reduce the amount of polymer. Some polymer nano-composites have special physical properties, e.g. magnetic behavior, electric conductivity and non-linear optical property [76].

Preparation and processing of nano particles of metal sulfide such as zinc sulfide, cadmium sulfide, lead sulfide and their composites are very interesting. The immobilization of these nano particles on polymer through several new techniques includes surface modification and in situ polymerization.

Tab. 2. Different type of thiols compounds used in ophthalmic lens applications.

Thiols Compounds	**Structures**
Dithiols	$HSCH_2CH_2SCH_2CH_2SH$ 2-mercaptoethyl sulphide  4,4'-thiobenzene thiol
Trithiol	 4-mercaptomethyl-3,6-dithia-1,8-octanedithiol
Polythiols	 1,2- thiobis-(2-mercaptoethylthio) -3-propane thiol  Pentaerythritol tetrakis (3-mecaptoacetate)

The properties of resulting polymer are enhanced by nano particles. Nano-CdS-polythiourethane (PTU) composite particles (CdS-PTU) were prepared, via preparation of nano-CdS in a reverse micellar system followed by surface-modification with thiol molecules, and polymerization by polyaddition of hexamethylene diisocyanate (HDI) and dithoils (xylene-a,a'-dithiol: XDT) or 4-

hydroxythiophenol (HTP) in the presence of the surface modified nano-CdS. The effects of thiols used as the surface modifying agent and polymerization of monomer were investigated, on stability of CdS-PTU for photo-irradiation during photocatalytic H_2 generation from aqueous solution of 2-propanol. The composite more dispersed containing nano-CdS had improved photo catalytic properties, which were found to have been affected by employing benzyl mercaptan as the surface modification agent for nano-CdS, and HTP as the monomer [77].

The refractive index of polymer system can be increased by addition of lead sulfide whose refractive index is 3.88. Refractive index of nano composite is of special interest, since material could be used for the development of novel solar cells [78].

Thiol based monomers

The different types of thiols that are used for optical applications are shown in Table 2. The high reactivity of the thiol group present several possibilities to design novel chemistries meeting requirements of various optical applications a) redox resins b) ion exchange resin, c) heavy metal ion absorber d) anti radiation agents [75], e) unblocking agents [77] f) Hydrolysis Catalyst [77] g) Substrate in graft copolymer synthesis [78] h) antioxidant i) Cross linking agent in rubber j) high refractive index monomer for optical application.

Jha et. al. [79-81] synthesized polythiol can be used as monomer in optical lenses, chain transfer agents for polymethacrylates, as curing agents for epoxy resins [82], natural and butyl rubber, consumer and industrial adhesive, coatings, sealant, antioxidant for polyolefins, and low temperature plasticizer for synthetic rubber.

The transparent plastic easily obtained by polyaddition of polythiol and polyisocyanate and has high refractive index and high Abbe number [29-31].

Sulfone based monomers

Both aliphatic and aromatic polysulfone have important applications. Polyarylene sulfones belong to the class of high performance engineering thermoplastics that retain useful optical properties up to about 200 ^{0}C, exhibit good transmittance and high refractive index. Their thermal and oxidative stability is due to the presence of sulfonyl group.

The polyaliphatic sulfones are synthesized by the reaction between olefins and sulfur dioxide shown in Figure-5. Radical generators such as oxygen, peroxides, or azo compounds initiate the polymerization. Several metal salts such as silver nitrate sulfite, & sulfate or lithium and ammonium nitrate have also been found to be excellent catalysts. This type of polymerization process allows only the formation of polysulfone containing two carbon atoms between the sulfone groups. The product have rather low thermal stability and are sensitive towards bases. For these reasons such polymers, have not found widespread commercial utilization [83].

By Friedel- Crafts polycondensation (1965) of aryl sulfonyl chloride aromatic polysulfones were obtained. This product has excellent thermal and chemical properties. Polysulfone polymers are a family of engineering resins that combine transparency along with exceptional performance attributes to deliver unique advantages for various applications. In the natural state, sulfone polymers are transparent but not completely colorless. Polysulfone polymers have the highest heat deflection temperature of any amorphous polymer; which therefore make it suitable for high-end applications such as visors of space suits.

Polysulfones have a high refractive index of 1.634 – 1.675 and are desirable for many lens applications as they allow for thinner and higher power lens. Aromatic polysulfone a & b in Figure-6 prepared lenses which had superior moldability, thermal stability and impact resistance [84].

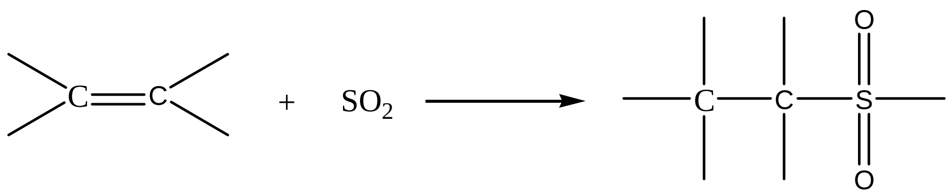


Fig. 5. General reaction of polysulfone.

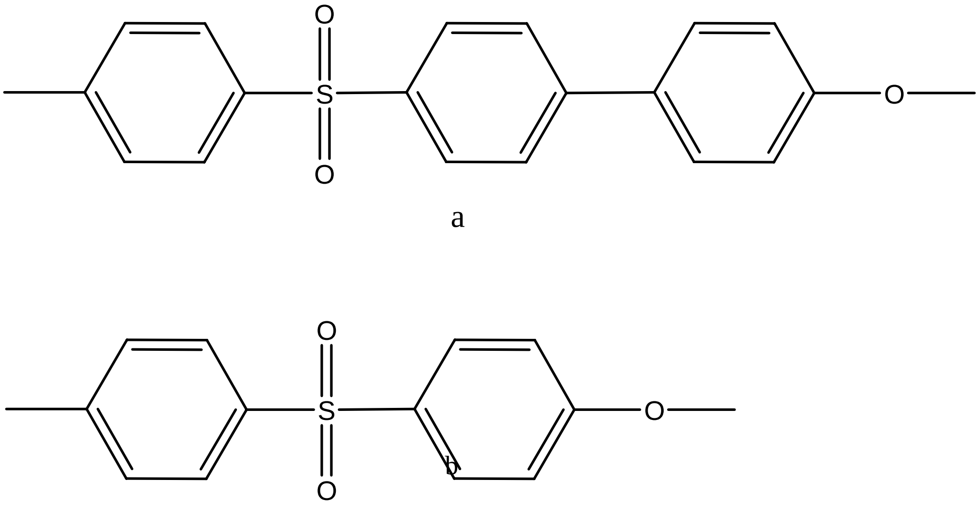


Fig. 6. a and b are aromatic polysulfones.

Sulfide based monomer

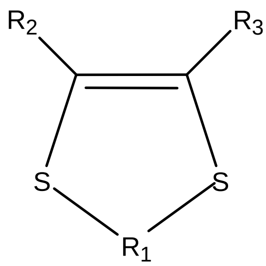
During the last several decades the synthesis of polymer with high sulfur content was carried out with the aim of improving chemical stability, visco-elastic and optical properties. Polymers that are structurally closest to polysulfur are polysulfide, which contain various units R; where R is alkylene, oxyalkylene or arylene group. The general formula of polysulfide is-

$$[\text{ ----R-S}_x\text{----}]_n \quad \text{where x \& n = 1, 2, 3,---}$$

Remarkable progress has been made recently on the synthesis of polysulfide polymers by different routes, such as ring opening polymerization of cyclic polysulfide as well as addition and condensation polymerization of elemental sulfur [84]. Using sulfide based material in a copolymer having a high refractive index (> 1.55) and large Abbe no. (≥ 32) is suitable for use as eyeglass lenses [85].

The optical resins are also obtained from aromatic polysulfur copolymers with structural and reduced superior moldability, thermal resistance and impact strength [86-90]. Okazaki et.al. prepared polysulfide – based resin by curing the compound having a high refractive index, low dispersion properties and good heat resistance, impact resistance and scratch resistance. These were mixed with a catalyst and internal mold releasing agent, degasified at room temperature under reduced pressure, charged into a mould and heated at 70 – 120 °C for 20 h to give a resin with refractive index 1.594 and Abbe No.46 [91]. Polymerizable compounds described by Ryu et al. [92] are useful for the production of eyeglass lenses.

The optical material, suitable for use in making a plastic lens, comprising a polymer substrate was obtained from the polymerizable compound containing a compound having ≥ 2 episulfide groups in the molecule and hard coat containing an UV absorbing agent. Material was injected in mold and polymerized for 24 hours while the temperature was gradually varied from 30 °C to 120 °C for obtaining a lens substrate [93].



R_1 = unsubstituted C 1-3 alkyne

C 4-7= cycloalkane, C 3-7 = Heterocycle
C 6-10 = aromatic

$R_{2,3}$ = $SSCH_2TH$, SSTH where TH = thiernyl

Fig. 7. General structure of sulfide based monomer.

Sulfide or disulfide compounds useful for light resistant optical materials such as lenses, prisms, optical fibers, etc. contain sulfide or disulfide compounds bearing epoxy and / or episulfide groups, benzotriazole type UV absorbents. Thus, mixing a mixture of bis–(2,3–epithiopropyl) disulphide and 2–(5–methyl–2 hydroxy phenyl) benzotriazole with N,N-dimethylcyclohexylamine at a reduced pressure for 0.2 hour and cast molding at 120 °C for 24 hours gave a refractive index approx 1.744 T_g 105 °C transparency 24% and good light resistance [94]. Wang et.al. has claimed a optical material useful as ophthalmic lenses comprising of polymers manufactured from Figure-7. This compound was polymerized in a mould to give lens showing refractive index1.772 and Abbe's no. 30.6 [95]. Disulfides having 1-4 thiirane disulfide groups in a molecule are manufactured by reaction of $QSSCO_2$ R1 (Q= thiirany; R1=C1-10 aliphatic alkyl, C5-8 aliphatic cycloalkyl, aromatic group) with mono to tetrafunctional thiols. Polymerization of CH2 (SSQ) 2 in a mould gave a lens showing refractive index 1.79 and Abbe no.28 [96].

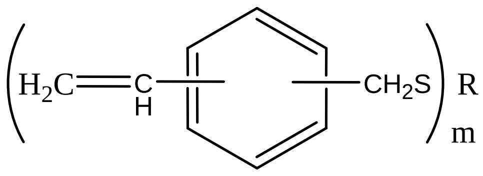
Yoshimura et. Al. prepared novel episulfides based optical materials; heat and impact resistant polymers with refractive index 1.67 and Abbe no. 34 [97].

Vinyl based sulfur-containing monomers

Diethylene glycol bis(allyl carbonate) (CR-39) is a common vinyl based resin. It has a proven performance of good impact strength, superior abrasion resistance, easy tintability and low refractive index. Therefore, incorporation of sulfur containing monomer may be useful to increase refractive index. A resin based on a polyene-polythiol reaction can be formed with a high productivity because monomers can be rapidly polymerized via a radical reaction, though it has disadvantages such as a high volume shrinkage percentage making a precise casting polymerization difficult. In addition, as for physical properties as a resin, it is generally brittle, which, of course, limits its applications. Furthermore, the refractive index of the resin can be improved by increasing a content of a thiol component in the monomer composition. However, as the content of the thiol component increases, a resin prepared by polymerization increasingly becomes rubbery and thus cannot be used for an optical product [98]. Odorless, impact resistant resins have been obtained by Yihiro et.al. from sulfur–containing ally carbonates. A polymer prepared by heating diethylene glycol bis(allyl carbonate), HC: CH CH_2 O_2 C $(SCH_2\ CH_2)_2$ S CO_2 CH_2 CH: CH_2, and diisopropyl peroxydicarbonate had refractive index 1.6 and high impact strength [99]. Diethylene glycol bis allyl carbonate mixed with polythiol in different ratio and polymerization was carried out by Jha et. al. with toluene diisocynate in the presence of dibutyl tindilaurate. Transparent plastics whose refractive index varies from 1.59 to 1.65 and Abbe number from 28 to 32 has been reported [100].

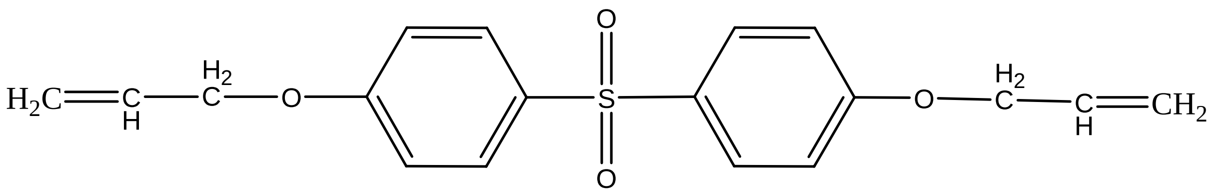
Wada et.al. prepared prepolymer by radical polymerization of mixture of divinyl benzene, ethyl vinyl benzene, and diethyl benzene in the presence of 2–mercaptoethyl sulfide. They also obtained urethane solution by heating hexamethylene diisocyanate with mixture of 2,2 bis[3,5–dibromo–4–(2–acryloxyethyl) phenyl] propane, 2–[2,6–dibromo–4–(3,5–dibromo–4–(2 hydroxy ethoxy)–2,2-dimethylbenzyl] phenoxy] ethyl acrylate, 2,2–bis[3-5–dibromo–4 –(2-hydroxy ethoxy) phenyl] propane. Molding this urethane solution with prepolymer gave lenses having refractive index 1.614 and good impact strength [101]. Polymers useful as optical materials with high refractive index, good light resistance, Abbe No., transparency, hardness and dyeability and low odor during processing have been prepared from monomer containing ≥ 2 SH groups and monomers containing ≥ 2 –vinyloxy and/or vinylthio groups [102].

A vinyl benzylthio compound is found to be producing plastic lenses having high refractive index (1.65) low specific gravity (1.19), excellent heat resistance and processability [103]. A lens was prepared from bis(2–mercaptoethyl) sulfide, divinylbenzene, ethylvinyl benzene, glycidyl methacrylate, and pentacrythritol tetracrylate and pentaacrylthritol triacrylate [104]. Kuwata et. al. comprise lenses with low sp. gravity, good dyeabilty, resistance to heat and impact etc. by curing mixture containing polythiol, divinyl benzene and/or divinyl phenyl, 3-iso phenyl-x, x-dimethyl benzyl isocyanate and optionally vinyl monomer. Thus monomer were mixed with radical polymerization initiator and catalyst, cured in a mould and further processed to give test plate showing light transmittance 90%, refractive index (25 °C) 1.658 and Abbe no. –33 [105]. Figure-8 shows the general structure of vinyl based sulfur-containing monomer used for optical applications.



m = 2-3; R = m-fold substituted hydrocarbon chain
3 to 6 carbon atoms containing one bivalent S atom,
with one OH group.

a



b

Fig. 8. a & b are general structure of vinyl based sulfur containing monomer.

Acrylate based monomers

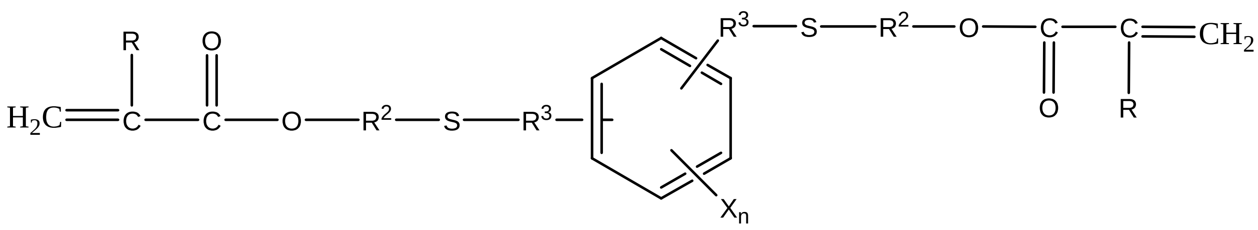
Recently, there has been a demand for a resin having higher strength and impact resistance. Thus thio(meth)acrylate is to provide an optical resin composition that can be rapidly polymerized. Thus it exhibits good handling properties, excellent optical properties, particularly a high refractive index and excellent impact resistance and also generates less unpleasant odor during processing. This is used as an optical device such as lenses for eyeglasses and cameras, as well as a transparent resin for a variety of applications. Furthermore, a lens prepared with the optical resin, if necessary, subjected to physical or chemical treatments such as surface abrasion, antistatic treatment, hard coating, anti-reflection coating and dyeing, for improvements such as prevention of reflection; improvement in hardness, abrasion resistance and chemical resistance [106].

The polymerization and co-polymerization of vinyl thioacetate in the presence of radical catalysts does lead to high molecular weight because its exhibits a high chain transfer constant [107]. Subsequent hydrolysis of the thioacetate functional group requires alkaline conditions and is accompanied by oxidative crosslinking [108]. Copolymerization of thioacetate with vinylene carbonate [109], methylmethacrylate [108-111], N-vinyl succinamide [109], N-vinylphthalamide [109], N-vinyl carbazole [109], styrene [108-111] and methacrylate [111] led to high refractive index plastic.

The process for preparation of novel sulfur-containing O-(meth) acrylate compound included the dithioacetalization, thio-esterification or thiourethanization of a novel thiol compound followed by dehydrohalogenation, for optical resin composition. In general, a resin produced may, however, have inadequate strength or impact resistance, that is, it may be brittle and breakable.

The resins for optical lens were prepared by Sugio et. al. by the copolymerization of monomers chosen from unsaturated esters, carbonate and ethers of and other co-monomers. Thus 4,4'–thiodiphenol dimethacrylate, chlorostyrene, and benzoyl peroxide were stirred at 60 °C for 1.5 h, cast into glass cell and heated at 80 °C for 12.5 hrs to give a transparent lens with refractive index 1.610 and Abbe No.30 [112]. Eyeglass lenses are prepared with a copolymer comprising methacrylthioester 30-60, triethylpropane tris(2–mercapto propionate) and methacrylic acid ester. The lens obtained from the copolymer showed refractive index 1.648, Abbe No.29 and density 1.39 gm/ml [113]. Optical lenses with high refractive indexes are prepared from a mixture benzene thiol dimethacrylic thioester), di(meth)acrylic esters (eg. diethylene glycol diacrylate), thiodi(mercaptoethyl) and aromatic vinyl compounds (e.g. styrene). The lens had a refractive index of 1.642 [114]. Optical lenses with high refractive indexes are also prepared from a mixture containing methacrylic thioesters (4,4'–thiobisbenzene thiol dimethacrylic thioester), pentacrylthritol tetrakis (thioglycol), thiodi(mercaptoethyl) and divinyl benzene parts. The lens had refractive index of 1.654 [115]. The compound with long pot life comprise thiol(meth)acrylates, polymerization initiators and 4,3,5 – HO (Me$_3$ C)$_2$ C$_6$ H$_2$ CH H$_{2n+1}$ (n = 1 – 3) and they polymerized to give lenses [116].

Schmitt et. al manufactured highly transparent methacrylate copolymers for optical lenses. Thus, by stirring methacrylic acid anhydride with Na 1,2, ethandithiolate in ethyl acetate/water mixture at 35 °C gave a reaction mixture that was purified, stabilized with hydroquinone monomethyl ether, stirred and filtered to give a clear, colorless ester solution. This was combined with diisocyanate, dithiol, methacrylate and stirrer for 1-5 h at 60-80 °C and polymerized with AIBN to give refractive index 1.6069 Abbe No. 37.2 and impact strength 3.85 KJ/M2 [117]. Okuma et. al. prepared (Meth) acrylic acid thioesters andthe manufactured optical part had good transparency, impact resistance and refractive index [118].



R^1 = H, Me; R^2, R^3 = C$_{1-12}$; X = Halogen other than F; n = 0-4

Fig. 9. General structure of acrylate based sulfur containing monomer

Isocyanate/Isothiocyanate based monomers

The reaction between an isocyanate/isothiocyanate and a compound containing active hydrogen is generally considered to take place by attack at the electrophilic carbon atom of the isocyanate group. The relative rates of reaction of different compounds with this group depend on the nucleophilicity of the reactive centre in the attacking compound. The rate may be adjusted to a desired level by adding a known reaction catalyst useful in the manufacture of polyurethane. Polymerization method, in which the polymerization conditions are suited to polythiol compound having a higher reaction rate with an isocyanate/isothiocyanate compound, the initial polymerization temperature is set at low temperature and that temperature is gradually increased with increasing time. The optical material formed of polythiourethane obtained by subjecting a polyisocyanate/isothiocyanate compound and a component comprising two or more of hydroxyl groups or mercapto or both groups to polyaddition reaction [119-120]. Table-3 shows the different type of isocyanate and isothiocyanate compounds, which are used for optical applications. The polythiourethane base resins have high refractive index, low dispersion characteristics and high Abbe's number. This lens has excellent impact resistance, heat resistance, scratch resistance, weatherability, and less optical distortion [121-123].

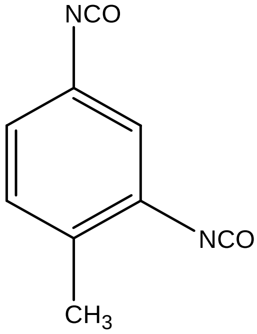
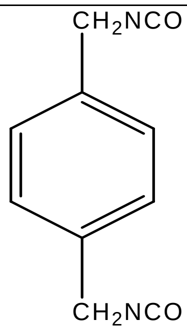
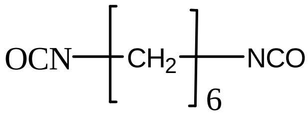
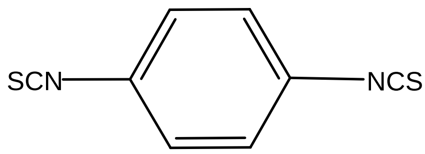
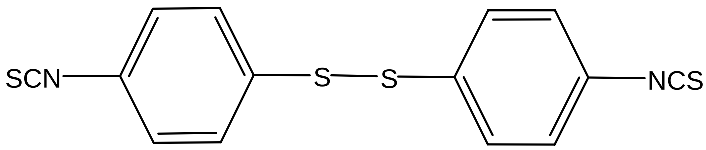
In the manufacture of polythiourethane lens, polymerization is usually required to be carried out for short time in order to obtain the optical and strain free lens, which is satisfactory as the plastic lens. Therefore, these resins are extremely useful for industry. In addition, the surface of this lens is too soft and can be scratched, therefore, it is necessary to apply protective coat onto the surface of this lens [124]. Additional optical properties are transmittance, coloration, hardness, machinability and processability. This resin can be used for an optical material such as a plastic lens, a prism, an optical fiber, a filter, as a glass, a vase, a substrate for an information recording medium and light emitting diode [125].

Novel polythiol having four or more functional group are prepared by reacting thiourea with thiol compounds to form isothiouronium salts and hydrolyzing them. Sulfur containing polyurethane is prepared by the treating polythiol with polyisocyanates. The polyurethanes have a high refractive index and low dispersion of refractive index, are light weight, colorless and transparent, have no optical distortion and have excellent weather resistance, dye affinity, heat resistance, impact resistance and machinability [126].

Kim et. al. obtained polythiourethane (PTU) from the combination of ESTT with each of 4,4 methylene bis(phenyl isocyanate) (MDI) Toluene 2,4-diisocyanate (TDI), isophrone diisocyanate (IPDI), m-xylene diisocyanate (HMDI) in the presence of dibutyl tin dilaurate as a catalyst, in casting mould; characterized by FT-IR spectroscopy and elemental analyzer for sulfur analysis. Their thermal, mechanical and optical properties were investigated by using DSC, TGA, hardness tester and refractometer. PTU with T_g above 110 °C showed good hardness (shore D) in the range of 86-89. The optical transmittance of amorphous PTUs through UV-visible source in the range of 400-600 nm was good. PTUs showed refractive index above 1.66 and their refractive index gradually increased with increase of sulfur content [127].

The polymers, useful for lenses are manufactured by reaction of a compound containing 1,2,7-trimercapto-4,6 dithioheptane, m-xylene disocyanate, a catalyst, a UV absorber and a release agent was cured to give a plastic showing lenses refractive index 1.681, Abbe no. 32, heat distortion temp 91 °C and good impact resistance [128]. Cast polymerization > 1 polyiso(thio)cyanate with $HSCH_2CH$ (SCH_2CH_2SH) CH2SH, respectively gave resins, useful for heat resistant lenses with high refractive index and low dispersion properties [129]. Molded sulfur – containing urethane resins were manufactured by polymerization of groups containing isothiocyanates, polyols, polythiols and hydroxythiol in the presence of phosphoric acid O – alkyl esters in a mould. One such resin was made from SCN $(CH_2)_4$ NCS and C $(CH_2\ SCH_2\ CH_2\ OH)_4$ in the presence of O – methyl phosphorothioate. The resin product was transparent with haziness (0.1%) [130].

Tab. 3. Different type of isocyanate/isothiocyanate compounds used in ophthalmic lens applications.

Isothiocyanates and Isocyanate Compounds	**Structures**
Isocyanate	 Toluene diisocyanate  Xylene diisocyanate  Hexamethylene Diisocyanate
Isothiocyanate	 Benzenediisothiocyanate  Dithiobis(4-isothiocyanato phenyl)

Polymerization of sulfur containing monomer

The popularity of plastics lenses in the ophthalmic market has increased greatly in recent years. Now, thermosetting optical resins and their monomers which are put to practical use for a lens for eyeglasses and the like can be substantially classified into two types; a polycondensation type represented by a polythiourethane resin and a radical polymerization type represented by an acrylic or vinyl compound. A polymer can be prepared by rapid polymerization by means of either UV rays or thermal or both.

Thermal Polymerization

Thermal polymerization is an exothermic chain reaction; problems of heat removal frequently arise during polymerization of materials. The propagation step in the polymerization of unsaturated compound results in the conversion of one double bond into two single bonds, it is highly exothermic. Although the overall heat of reaction is the sum of the contribution of different reaction steps such as chain initiation, propagation and termination; the major portion arises from the propagation reaction. The effect of temperature on the polymers resulting from uncontrolled reaction has undesirably low molecular weights and wide molecular weight distribution. Discoloration occurs due to side reactions. Condensation reactions are only mildly exothermic and proceed not by chain mechanism, but by a step mechanism in which each step requires the same activation energy. Therefore, linear condensation polymers frequently have low melt viscosity, which facilitate heat removal and escape bubbles. Consequently, even with large quantities reacting without stirring at temperature over 200 ^{0}C there is no danger over heating [131]. Some examples of thermal polymerization is given below:

-Vinyl based sulfur-containing monomers

A mixture of pentaerythritol tetrakis (B–thiopropionate) and 1,4–bis(vinyl thio) benzene containing 1% tert–butyl peroxy 2–ethyl hexanoate was polymerized at 120 °C for 24 hours and 120 °C for 4 hours to give a copolymer having refractive index 1.623, Abbe No.31 and no odor [132]. Honda et. al. prepared a transparent lens by radical polymerization of a compound (H S CH_2 CH_2 $CO_2)_3$ C C_2H_5, benzene and benzoyl peroxide by casting between two glass plates and heated with linear temperature increase at 60 °C for 24 hours, 80 °C for 5 hours and finally at 90 °C for 5 hours to give a transparent lens showing refractive index 1.615, Abbe no.29 and density 1.23 g/cm^3 [133].

-Acrylate based sulfur-containing monomers

The bis(2–mercaptoethylene thiomethylene) benzene dimethacrylate, xylene diisocyanate and pentaerythritol tetrathioglycolate 13.4% were mixed in mold and polymerized at 80 °C for 6 h and 115 °C for 10 h to give a lens showing good moldability, heat resistance and thermal decomposition temperature 100 °C [134]. A compound comprising 1,4–bis(2–mercaptoethylene methylene) benzene dimethacrylate, 1,4–bis(2–mercaptoethylene thiomethylene)benzene, α-methylstyrene and initiator was heated in a glass mold at 120 °C for 17 hours to give a lens with good drilling property, energy absorption 46 K^{-m} and n 1.650 [135].

-Isocyanate/Isothiocyanate based monomers

The styrene, p–mercapto methylstyrene, 1,3–xylene–diisocyanate and dibutyl tindilaurate were treated at 60 ° for 5 hours mixed with AIBN and heated at 50 – 130° for 15 h in a mold to give a test piece with refractive index 1.61 and density 1.21 g/cm^3 [136]. The bis(2–mercaptoethylene thiomethylene) benzene dimethacrylate, xylene diisocyanate and pentaerythritol tetrathioglycolate were mixed in mold and polymerized at 80 °C for 6 hours and 115 °C for 10 hours to give a lens showing good moldability, heat resistance and thermal decomposition temperature 100 °C [137].

Photo-polymerization

Photo-polymerization techniques are sometimes called stereo lithography. The polymerization involves formation of covalent bonds rather than intermolecular van der Waals interaction, [138-141] photo-polymerizable materials often shrink during curing. Shrinkage of polymer is the primary limitation of the dimensional stability of stereolithography. Thickness of the laminar layer is determined by both the need to reproduce fine detail in the object and by the penetration depth of the actinic laser light into monomer bath. Photoinitiated polymerization can be used to replicate microstructure surface having high degree of precision and extremely high dimensional stability both during and after the curing process. The shrinkage problem is rectified if the cross linking density is too high. Examples of photo-polymerization are given below:

-Vinyl based

Dggins et. al. prepared crosslinking olefin – thio polymers useful for video disks, ophthalmic lenses etc. The polymer prepared from 35-85% olefin monomers and 15-60% polythiol compounds. Thus a 60:40 mixture of divinyl benzene and pentacrythiol tetrakis(3–mercapto propionate) was cured in mold by UV – radiation to give plates [142]. Jha et. al. polymerized diethylene glycol bis allyl dicarbonate (CR-39) by gamma radiation and achieved transparent, better scratch resistance property without affecting refractive index of polymer [143].

-Acrylate based

A mixture of thio(meth)acrylates, ethoxylated bisphenol A dimethacrylate, 2–(tribromophenyl) oxylethyl acrylate, Ph methacrylate, Irgacure–184, and diphenyl (2,4, 6–trimethyl benzoyl) phosphine was exposed to UV light (80 w/cm^2) for 3 min on each side to give a sheet with transmission 91%, refractive index 1.5910, Abbe No.43.5 density 1.2713 and good surface appearance and temperature resistance [144]. The compounds are manufactured from, 1,2–bis[(2–mercapto ethyl) thio]–3–mercaptopropane and (meth)acrylyl chlorides. A mixture of 1,2–bis[(2–mercapto ethyl) thio]–3–mercaptopropane and NaOH in Me_2CO was treated dropwise with β -chloropropionyl chloride, then treated at 10 °C for 4 h to give copolymer (R = H). Both homo-polymers and co-polymers manufactured transparent by UV polymerization gave wear resistant lens [145].

Optical materials are composed of polymers obtained by curing compounds containing p–bis(β-methacryloxyethylthio)xylene, bis(methacryloyloxyethyl) phosphate, styrene, benzophenone and perbutyl part were mixed, defoamed, poured into a cavity; the irradiated product showed refractive index 1.595, good surface precision and good transparency [146]. The feeding of the mixture irradiated by UV and heating the product at 100 °C for 2 hours gave transparent lenses having refractive index 1.595 [147].

-Urethane based

A compound containing bis(2–acryloyl thioethyl) sulfide a pre-polymer prepared from HS CH_2 CH (S CH_2 CH_2 SH) CH_2 S CH_2 CH_2 SH and xylene diisocyanate] and 2–hydroxy–2–methyl 1–phenylpropane–1–one, was poured into a mold and cured by

UV irradiation to give a lens having refractive index $\geq$ 1.65, Abbe No.35, good heat and impact resistance, transparency and dyeability [148].

Casting process of ophthalmic lenses

In casting process liquid or powder is used as starting material that is shaped without the application of significant pressure. The absence of pressure means that the mold and support equipment used in the casting does not need high pressure in molding process such as injection molding. Mold for casting can be made of wood, plaster, plastic, aluminum, rubber and other materials that may fit specific applications. Heat is sometime added to hardening, although this is not required in all cases. The application of heat depends on the type of resins being cast. Materials can achieve the solid state by chemical reaction, by external heating followed by cooling or by solvent evaporation. The most common types of materials used in casting are liquid resins namely monomer, syrups or low molecular weight thermosets. These materials are hardened through some chemical process, usually polymerization or cross-linking [149-152].

In casting process a liquid is poured into a mould and allowed to react, cure or harden. Many resin systems may be utilized in this process, e.g. acrylic, diethylene glycol bisallyl carbonate, polythiourethane, epoxy, phenol-formaldehyde, polystyrene, polysulfide and silicone. Cast articles provided, high transparency, a wide range of colors, rigidity, moderate impact strength, thermal and chemical resistance and excellent weatherability. The sheet was used in vast variety of applications such as glazing for aircraft, architectural, automotive, mass transit and security, signs, displays, sanitary ware, lighting fixtures, decorative panels and different type of lenses. The monomer-based formulation was poured into mould or “cell” consisting of two flat sheets reported by an electrometric material or gasket around the periphery. After removal of the residual air with the filled mould the mould was sealed and the monomer mixture was polymerized in the presence of heat or photo initiated or electron beam radiation. The cast sheet becomes known as organic glass [153].

In casting monomer type resin system the key factors requiring prevention of entrapped or internally generated bubbles or voids, supply and removal of heat or light energy, rate of resin cure or polymerization, shrinkage and adhesion of resin to the mould surface. These factors depend on the resin formulation, the size, thickness and complexity of mold, and the optical and structural requirements of the finished articles [153].

Casting is the most common ophthalmic lens [154-155] production method in use today. It consists of placing some chemicals between two glass metal moulds held apart with flexible gasket, than subjecting to heat or UV energy. Some Manufacturers use water bath because of improved heat conduction. Figure-10 show mould assembly of lenses and Figure-11 shows block diagram describing the lens casting process. The thiol containing compound [156-159] and unsaturated compound are useful for casting process. Mold assembly is suitable for forming the ophthalmic lenses or the lens blanks, which is produced by the cutting and polishing operation. The mold assembly has a structure, which assures a high degree of forming accuracy and is economical to manufacture [160].

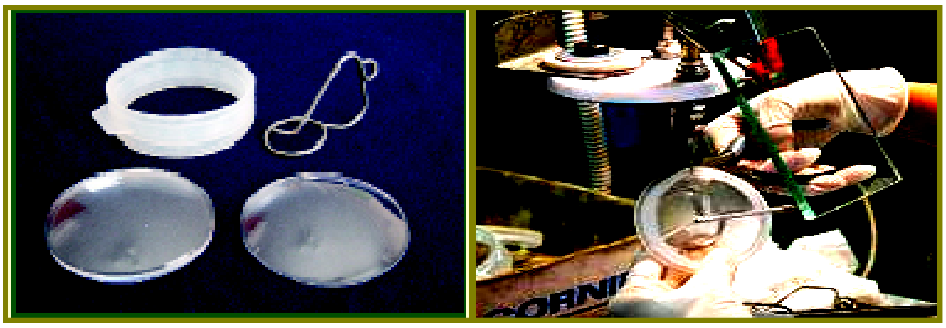


Fig. 10. Gasket, glass mould, clamp and filling unit of lenses.

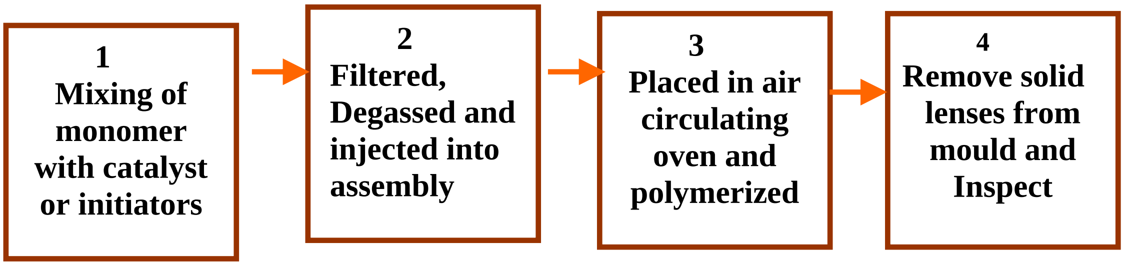


Fig. 11. Block diagram describing the lens casting process.

Prevention of air bubbles and voids

Entrapments of air bubbles due to the casting operation depend on the viscosity and surface tension of the monomer formulation, solubility of air in the monomer mixture and design of the mould.

High speed mixing and vortexing should be avoided during preparation of the casting formulation. Vacuum may be applied to the liquid before filling mold to remove entrapped air. Careful pouring or pumping of the liquid mixture into the mould minimize the formation of air bubbles, which also prevented heating of the monomer mixture to reduce viscosity, adding surfactant to decrease surface tension, applying mechanical vibration, or subjecting the casting to high pressure. In autoclaves the boiling point of the monomer is raised, thus permitting the use of higher temperature with minimum bubbling and shorter cure time. Careful selection of the casting formulation and close control of the polymerization can prevent internally generated bubbles or voids during the polymerization process [161].

Polymerization Control

In the casting of thin sheet with a high ratio of surface area to total volume the temperature can be easily controlled. Heat generated during the polymerization of monomer system can be dissipated rapidly, for example, by external cooling.

Casting with a low ratio of surface area to total volume such as cube or block, do not absorb or dissipate heat rapidly. A large temperature gradient from the centre to the outer surface area can result in high internal stress, reduced dimensional stability, and potential carrying, cracking or voids. Control of the rate of heat evaluation is critical. For every temperature rise of 10 °C the polymerization rate of resin doubles [162]. Proper selection of catalysts, optimum time and temperature process cycles and selection of mould materials may accomplish control. In massive castings complete monomer reaction is attained slowly at room temperature and raising the temperature completes curing.

Comparison with and without sulfur containing monomer

Sulfur containing plastics such as 2,4,6-triisothiocyanato-[1,3,5]triazine and 1,3,5-benzene trithiol polymerized to form polymer with refractive index 1.80 [163]. The refractive index of different types of plastics without and with sulfur atoms are shown in Table-4 and Table-5 respectively. Sulfur-containing plastics have high refractive index compared to that without sulfur containing plastic. So, sulfur-containing plastics are suitable for optical materials and ophthalmic lens applications.

Tab. 4. Without sulfur containing monomers.

Materials	Refractive Index
Diethylene glycol bis allyl carbonate	1.498
Diallylphthalate	< 1.57
Allyl benzoate	< 1.57
Benzyl methacrylate	< 1.57
Bisphenyl compound	< 1.60

Tab. 5. With sulfur containing monomers.

Materials	Refractive Index
Diethylene glycol bis allyl carbonate and Polythiol/unsaturated thioester[100]	< 1.65
Polyisocyanate and Polythiol[128]	< 1.68
Sulfur containing methacrylate[112]	< 1.61
Sulfur containing aromatic vinyl Monomer[105]	< 1.65
Sulfide/Bisulfide/Polysulfide based monomer[96]	< 1.79
Polyisothiocyanate and polythiol[163]	< 1.80

Conclusions

The most important criteria for the selection of optical plastics for ophthalmic applications is high refractive index and high Abbe number. The challenging task is achieved by the incorporation of sulfur atom in polymer chain and meets desired refractive index and Abbe number which are required for thin and light weight lens. Various suitable candidates of sulfur containing plastics such as sulfide, vinyl, thio-acrylate and isocyanate/isothiocyanate are useful for optical applications. The current trend paved the way for sulfur containing plastics nowadays to be most popular in optical applications with improved optical properties.

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